bined with the α-amylose portion of corn starch are preferentially liberated. In all three cases the unsaturated acid radicals are the more easily removed. This result may be accounted for in two ways. It may be due either to a general lesser stability of compounds of carbohydrates with the unsaturated acids (oleic and linolic) in comparison with those of palmitic acid, or to the fact that these unsaturated acid residues are linked at positions different from that of the saturated one on the carbohydrate molecule. Position isomerism is known in the case of glucose derivatives to be the cause of differences in ease of hydrolysis.

Summary

1. The fatty acids associated with corn starch are hydrolyzed preferentially by acid, by base and by lipase-free amylase.

2. The linking between the unsaturated portion of the fatty acids and the carbohydrate is less stable to hydrolytic agents than that between the saturated portion and the carbohydrate.

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The Action of Aqueous Alkali on Starches, Amyloses and Modified Starches

BY T. C. TAYLOR AND G. M. SALZMANN[1]

The most common form of chemical change which starches or amyloses undergo gives rise to reducing sugars and is therefore probably a scission of glucosidic linkings. During the early stages of these transformations rather large changes in the physical aspects of the starches, or more particularly the pastes made from these starches, are obvious without any great accompanying changes in reducing value as measured by any of the common methods. By allowing the hot aqueous alkali to act on the sample, however, and then neutralizing and determining the new reducing matter iodimetrically by a modified Willstätter method,[2] it was found possible to magnify small differences among the starches and amyloses that would not be significant when based on the initial reducing value alone. This was possible because it was found that when any starch or amylose had an appreciable initial reducing value the aqueous alkali produced many times that amount after treatment.

While some inquiry was made into the nature of these reducing sub-

(1) This is an abstract of a dissertation by G. M. Salzmann, presented to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) (a) Willstätter and Schudel, *Ber.*, **51**, 78 (1918); (b) Goebel, *J. Biol. Chem.*, **72**, 802 (1927); (c) Kline and Acree, *U. S. Bur. Standards J. Research*, **5**, 1063 (1932).

stances, the main purpose of this investigation was to use this alkaline treatment followed by an iodimetric determination of reducing material as a means of discovering whether this behavior toward hot aqueous alkali is a property of the original amyloses or is due really to some altered material admixed with the amyloses either as they occur in the starches or as they are isolated after disrupting the granules. The technique was employed further to find the type of treatment which would have to be given a starch or amylose so that it would give subsequently some material susceptible to aqueous alkali.

It will be shown that when a starch or amylose is modified, apparently only a part of the original polysaccharide is changed, the unattacked portion remaining stable to the alkali. The altered portion is completely broken down by the alkali but the stable portion is substantially non-reducing and similar to glycogen in its resistance to hot aqueous alkali. Original starch or amyloses with no history of hydrolytic attack from aqueous acid, enzymes, etc., are unaffected by repeated treatments with hot aqueous alkali and the amyloid material after such treatments is still like the original qualitatively by any of the criteria such as specific rotation, blue color with acidulated iodine-iodide test solutions and quantitative production of glucose.

It has been well established by Nef[3] and Evans[4] that glucose and maltose are decomposed by aqueous alkali, giving ultimately numerous non-carbohydrate substances such as pyruvic and lactic acids, etc. Many of these substances consume iodine under the slightly alkaline conditions that obtain in the iodimetric technique[2] employed here. The amount of iodine used up, however, is always *much less* than that used initially to oxidize the aldose. The breakdown with alkali through the enediol form of the glucose or maltose gives, according to Evans, the new products and obliterates the original sugar.

On the other hand, while the attack of alkali also begins apparently at the reducing group in a degraded amylose, the iodine consumption is always *much greater* after the treatment with hot aqueous alkali than it was initially.

Since aqueous alkali might give decomposition products in some enol form which would give fictitiously high reducing values,[5] some of the material after decomposition of the degraded amylose was allowed to remain acidified for one hour before the iodimetric determination was made. There was no change in the amount of alkali consumed.

Combination of the alkaline treatment with the iodimetric titration after neutralization gives a rather unique method of attack on the problem, the

(3) Nef, *Ann.*, **357**, 294 (1907); **376**, 1 (1910).

(4) (a) Evans, Edgar and Hoff, THIS JOURNAL, **48**, 2665 (1926); (b) Evans and Hutchman, *ibid.*, **50**, 1497 (1928); (c) Evans and O'Donnell, *ibid.*, **50**, 2550 (1928); (d) Evans and Benoy, *ibid.*, **52**, 294 (1930); (e) Evans, *Chem. Rev.*, **6**, 281–315 (1929).

(5) Wolfrom and Lewis, THIS JOURNAL, **50**, 837 (1928); Hudson, *ibid.*, **52**, 2101 (1930).

iodimetric method for determining reducing substances avoiding effects of alkali that the Fehling method would introduce and measuring somewhat more of the decomposition products than the copper method.

In establishing the optimum conditions for the estimation of alkali labile material in starches and amyloses it was necessary to find the effect of concentration of alkali and time of treatment on them. Since the iodine consuming material produced by the alkali is in the main unknown, all results are expressed in milligrams of iodine per 100 milligrams of sample, except glucose and maltose. Here, usually, a weight was taken that consumed as much iodine initially as the particular starch or amylose with which it was compared. Due to the production of acidic substances during the decomposition with alkali, the total available alkalinity at low concentrations (0.025 *N*) in the volume of solution used was insufficient but larger volumes of the same normality gave the expected results. At higher concentrations there was no difficulty even with small volumes of reagent.

Experimental

Fifty milligrams of the dry sample was added to 2 cc. of water and to this mixture was added 2 cc. of a potassium hydroxide solution of such a concentration that the final mixture would have the desired normality with respect to the water. In a few cases where the total alkali was insufficient, 4 cc. of the aqueous alkali was taken but the normality of the mixture was fixed at the desired point by using the appropriate concentration of potassium hydroxide. The solution was placed in a large test-tube (8 × 1″) and the tube held in a boiling water-bath by a heavy asbestos board cover through which were bored holes just large enough to accommodate the test-tube. The test-tube was immersed in the water below the level of the cover, to a depth slightly greater than that of the contents of the tube. The purpose of this was to secure the maximum reflux action upon the walls of the tube. In *each case* the test-tube containing the alkaline mixture was heated for a definite selected length of time. At the end of the period the tube was removed from the bath, the contents transferred by washing into a 250-cc. Erlenmeyer flask, one drop of phenolphthalein solution[6] added and the solution neutralized with dilute hydrochloric acid.

For the titration, *N*/20 sodium hydroxide and *N*/40 standard iodine solutions were employed. As recommended by the Bureau of Standards[2c] the iodine and sodium hydroxide solutions were added dropwise in four alternate portions using 3 volumes of the alkali to 4 volumes of the iodine solution. An excess of 2 or 3 cc. of iodine and 3 or 4 cc. of sodium hydroxide solution was usually added and the mixture allowed to stand about five minutes so that the total time before the back titration was twelve to fifteen minutes. After acidification with *N*/5 hydrochloric acid the excess iodine was titrated with *N*/80 thiosulfate solution. The presence of sulfuric acid or sulfates always led to recurring end-points and inconsistent results.

When using glucose in similar experiments, the sample was 3.4 g. which by iodimetric titration reduced 4.3 mg. of iodine. This amount was taken because in subsequent experiments its behavior with hot aqueous alkali was compared with that of the particular corn beta amylose which had an

(6) Both the alcohol solvent and the phenolphthalein consume iodine so the minimum amount must be used. For very accurate work, say on glucose, it is better to use an aqueous solution of methyl orange which does not use up iodine [Mallen, *Analyst*, **54**, 244 (1932)].

initial reducing value of about the same amount. In this experiment, however, glucose and another corn beta amylose[7] were run.

The results are summarized in the graph, Fig. 1.

It is evident from the curve that there is always *more* iodine consuming material produced from the corn beta amylose than is initially present while with glucose there is always *less*. The maximum production from the amylose is with 0.1 *N* alkali while glucose is steadily decomposed at all normalities.

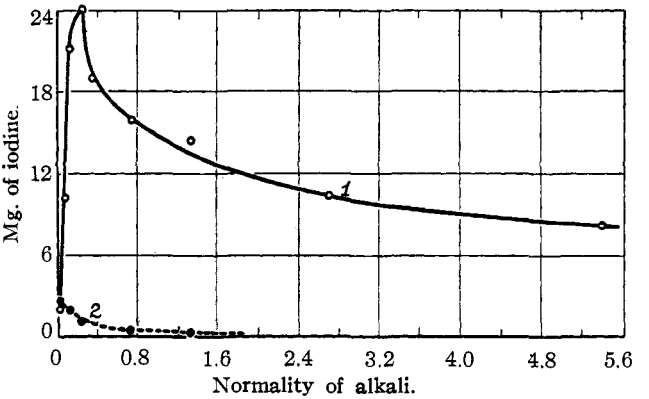

Fig. 1.—Reducing material expressed as mg. of iodine after treatment at normalities indicated: time constant at 15 minutes; Curve 1, corn beta amylose 100 mg.; Curve 2, glucose 3.4 mg.

To show that water alone has no effect, a sample of the beta amylose was treated for fifteen minutes and for two hours under conditions identical with the regular run but alkali was omitted. The reducing value was the same after the treatment as it was initially within the limits of the iodimetric determination.

Using 0.1 *N* solutions of potassium hydroxide a series of experiments was carried out on some corn beta amylose and on glucose in which the time of treatment was varied. This was done to see how the alkali effect changed when the treatment was prolonged beyond the fifteen-minute period. Each run was made for the specified time, the solution neutralized, cooled and the iodimetric titration made. The results are given in a graph, Fig. 2.

After a half-hour treatment the maximum amount of iodine consuming material is produced from this sample of corn beta amylose. Continued heating produces no more and after the one-hour period there is apparently some slight destruction of the reducing material already produced. On the other hand, glucose is decomposed to substances of less reducing value very early in the treatment.

(7) Taylor and Beckmann, THIS JOURNAL, **51**, 294 (1929).

Although the maximum effect of the aqueous alkali is noticed with the 0.1 N concentration, many of the subsequent experiments were carried out using 5.45 N alkali because it was desired to make comparisons with the results obtained by McBride,[8] who used that concentration on glycogen in a similar set of experiments (this is the concentration of alkali used in the Pflüger method for glycogen isolation from tissue).[9] While the magnitude of the effect is not as great as with 0.1 N alkali, it is in the same direction.

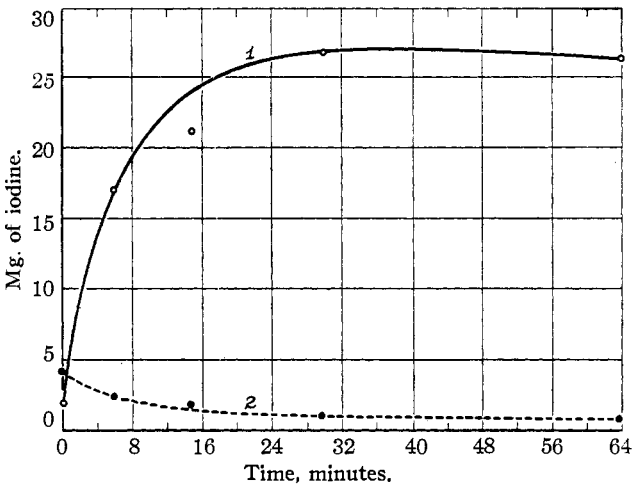

Fig. 2.—Reducing material expressed as mg. of iodine after treatment for periods indicated: normality of alkali constant at 0.1; Curve 1, corn beta amylose 100 mg; Curve 2, glucose 3.4 mg.

To find out what the tendencies were when other samples were run with the 5.4 N alkali the following materials were taken: (a) corn beta amylose separated from ground starch by the electrophoretic method,[7,10] (b) corn beta amylose separated from alcoholic-hydrochloric acid treated corn starch after gelatinization and rupture with ammonium thiocyanate,[10] (c) corn white dextrin made by heating moist acidulated starch. This material has a rather high initial reducing value of 4.1 mg. of iodine. (d) A mixture of 100 mg. of corn beta amylose as in (a) with an initial iodine reducing value of 2.0 with 3.4 mg. of glucose with initial reducing value of 4.3 to make the total 6.3. This was done to see if the method would discriminate between glucose and other reducing materials already present in the amylose. The complete record is shown in Fig. 3.

It is interesting to note that there is more alkali labile material in the beta amylose separated from the acid-treated, thiocyanate gelatinized corn

(8) J. J. McBride, Columbia Dissertation, 1929.
(9) *Arch. ges. Physiol.* (Pflügers), **93**, 81 (1903).
(10) Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

starch[10] than from that separated from the ground starch[7] or even a commercial white dextrin made by the dry heating of acidulated corn starch. As in previous experiments the glucose is quickly destroyed when alone and also when present with the beta amylose. After the first two minutes of the alkaline treatment the glucose is no longer a factor while the beta amylose runs its course as in the experiments without the presence of glucose.

These data point again to the fact that the initial reducing material in the amyloses and in the white corn dextrin is *not*, in the main, glucose.

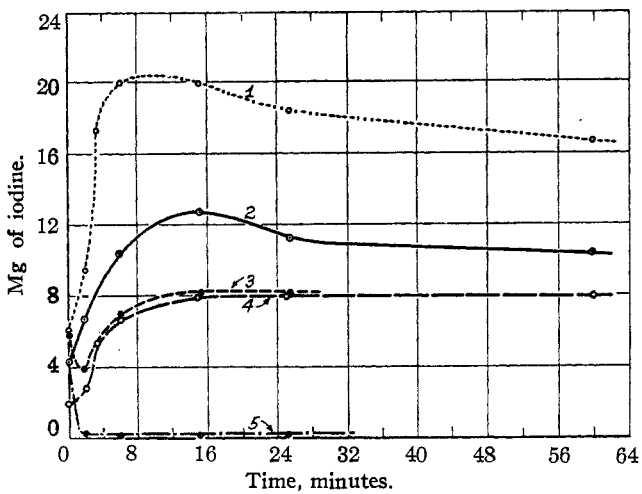

Fig. 3.—Reducing matter expressed in mg. of iodine after treatments of materials for period indicated with 5.4 *N* alkali: Curve 1, corn beta amylose from acid-treated thiocyanate-gelatinized starch; Curve 2, corn white dextrin; Curve 3, mixture of glucose, 3.4 mg., and corn beta amylose, the latter is the same material used in getting values in Curve 4; Curve 4, corn beta amylose from ground starch; Curve 5, glucose, 3.4 mg.; all amylose samples, 100 mg.

The reducing material present initially which is not glucose must be, therefore, closely allied to the amyloses and must have its source in them. It is probable that the reducing groups are the point of departure for the subsequent alkaline attack and the reducing material produced by this decomposition is substantially non-carbohydrate for it has no optical activity or other carbohydrate properties. In the absence of glucose the initial reducing value presages the amount of new reducing material which will be formed after the alkaline treatment.

That not all the starch or amylose is attacked by the alkali is shown by the fact that after neutralization of the alkali in any experiment, considerable quantities of starchy material may be precipitated by alcohol or, better,

acetone. This slightly yellow precipitate when redispersed in water gives a clear blue color with acidulated iodine–iodide test solution and has a specific rotation practically the same as that of the original amylose. On complete acid hydrolysis this alkali stable residue yields glucose, quantitatively.

Either the precipitation method or the hydrolysis to glucose and subsequent iodimetric determination of it may be used to estimate the amount of amylose which is not susceptible to the attack of aqueous alkali. When concentrated alkali is used the latter method is somewhat better since a small amount of salt is precipitated with the amylose by the alcohol or acetone.

Experimental

The Precipitation Method.—1.250 grams of starch or amylose was placed in a 250-cc. Erlenmeyer flask to which was added 30–35 cc. of water, this mixture usually being warmed until a paste formed. To this was added 15 cc. of 0.4 *N* potassium hydroxide, which made the final solution approximately 0.1 *N* with respect to potassium hydroxide. The flask was then placed in a beaker two-thirds full of water and heated in this water-bath at 100° for one hour. When using whole starches, it was necessary to keep them for one and a half to two hours at 100° with 0.1 *N* potassium hydroxide instead of one hour, since it usually required one-half hour for the thick paste to become limpid and only after the production of this thin dispersion due to gelatinization and rupturing of the granules, does the alkali destructive action occur as evidenced by the production of the yellow color. After this treatment the flask was cooled and the contents slightly acidified with 2 *N* hydrochloric acid. Due to slow evaporation, the total volume was usually about 10–15 cc. less than at the start. To precipitate any unattacked amyloses 100 cc. of ethyl alcohol was now added. Vigorous shaking helped in coagulating the colloidal material. When a yellow dextrin was similarly treated, it was found that acetone gave a quantitative precipitation, which alcohol often fails to do. After the material had completely coagulated, which in some cases occurred almost immediately, while in others several hours of standing were required, the clear supernatant liquid was decanted off, the residue transferred to a mortar, ground using two 15-cc. portions of alcohol and twice washed with ether. This dried residue was placed in the oven at 60–70° for ten to fifteen minutes to remove traces of ether and then weighed. This weight represents the recovered amyloses after an alkaline treatment. Precipitations of hot water dispersed starch or amylose without an alkaline treatment were made so that the percentage recovery could be determined by proportion. For this purpose 1.250 g. of starch was placed in an Erlenmeyer flask to which 40–50 cc. of water was added. A dispersion was again made by heating, alcohol was subsequently added and the precipitated amyloses dried and weighed.

The "Hydrolysis Method" for Determining Alkali Stable Residue.—Fifty milligrams of the starch was placed in an 8-inch test-tube and dispersed in 1 cc. of water, to which was added either 1 cc. of 10.4 *N* potassium hydroxide or 1 cc. of 0.2 *N* potassium hydroxide, so that the final concentration of alkali would be approximately 5.4 *N* or 0.1 *N* with respect to water as desired in each instance. The mixture was kept at 100° for one hour in the water-bath, then cooled and neutralized with 2 *N* hydrochloric acid. To hydrolyze the remaining amylose 5 cc. of 2 *N* hydrochloric acid was added, and the tube placed in the water-bath at 100°. It was found that hydrolysis was complete at the end of thirty-five minutes. The solution was cooled and neutralized with potassium hydroxide, and the reducing value determined in the usual way. This re-

ducing value consists of the sum of the reducing value due to the glucose formed by acid hydrolysis, and the reducing material left after the action of the alkali. It will be shown later that this treatment with acid does not produce any change in the reducing material already present from the alkali treatment. In order to determine the reducing value due to the glucose from the unattached amylose, it is necessary to subtract from the total value the reducing value due to the alkali treatment.

To avoid any error in the percentage of amyloses stable toward the alkaline treatment, it is also necessary to make conversions of the same amounts of starch or amyloses to glucose, but with no alkali pretreatment. Fifty milligram samples of starch or amylose were hydrolyzed with 5 cc. of 5 *N* hydrochloric acid for thirty-five minutes and the reducing value in milligrams of iodine found. Then the percentage of unaltered residue could be calculated on the basis of the ratio of the glucose from the residue to the glucose from the original starch or amylose.

By multiplying the weight of glucose by the factor 0.9 a weight is obtained which is recorded as starch.

The precipitation method and the hydrolytic gave results that differed among themselves on repetition on the same sample by about 0.75%, and with one another from 2 to 4%.

The amount of alkali stable material in the particular samples used in the above experiments seems to vary according to the source of the sample. From whatever source they appear to be similar in character and all show an iodine consumption of one or two milligrams, due probably to adsorbed reducing material from the solution out of which they were precipitated. When subjected again to the hot aqueous alkali no appreciable change takes place even after heating with 0.1 *N* alkali for three hours. This is evident for no reducing material is formed in the presence of alkali, the amount of residue after the alkali treatment is substantially the same after this second treatment as after the first and the specific rotation and iodine color are the same as for samples of original starch.

To get some clue to the type of treatment that might cause a part of the starch or amylose to be converted to alkali labile material, a number of starches, amyloses and modified starches were investigated. The initial reducing value was determined, they were subjected then to hot aqueous alkali, neutralized and the new iodine consumption noted, after which the amount of stable residue was estimated. The results have been arranged in order of decreasing amounts of alkali *stable* fractions (see Table I).

There is an inverse relationship between the initial reducing value and amount of amylose remaining after the alkali treatment. Some samples of starch have practically no alkali labile material in them while others have more. This is due very probably to the method of manufacture and possibly to agricultural conditions under which the starch was grown. Of the definitely controllable factors aqueous acid is the most potent in producing alkali labile material although other conditions such as grinding the starch in a ball mill also cause degradation of a part of the amyloses as the results under items G and H in Table I show.

TABLE I

STUDY OF FACTORS INVOLVED AND RESULTS OBTAINED BY ALKALI TREATMENT OF STARCHES AND AMYLOSES

Sample	% Alkali stable residue by alcohol precipitation method	Initial reducing value of orig. substance on 100-mg. samples, mg. of iodine	Reducing value after 5.4 *N* KOH 1 hr. at 100° on 100-mg. samples, mg. of iodine
Potato starch, Sample A	97	...	3.3
Corn starch, Sample B	90	...	5.1
Ground tapioca starch, Sample C	83	1.4	4.6
Ground potato starch, Sample D	75	...	8.2
Lintner's sol. starch, Sample E	74	0.6	7.2
Corn beta amylose, Sample F	73	2.0	8.0
Ground corn starch, Sample G	68	1.9	8.8
Reground corn starch, Sample H	67	2.6	9.9
Corn alpha amylose, Sample I	62	1.6	9.6
Ground corn starch, Sample J	59	3.0	11.6
Corn white dextrin, Sample K	56	4.1	10.5
Thin boiling starch, Sample L	56	4.7	12.9
Ground potato starch, Sample M	51	2.2	12.8
Corn beta amylose, Sample N	49	6.0	16.8

NOTES

Sample A represents a good grade of commercial potato starch. Sample B represents a good grade of commercial alkali-washed corn starch. Sample C represents a tapioca starch which has been ground for eighteen hours with quartz balls in a ball mill.[7] Sample D represents potato starch which has been similarly ground for 120 hours.[7] Sample E represents Lintner's soluble potato starch made by keeping potato starch in contact with dilute hydrochloric acid for six days at room temperature and washing twenty-two times with water.[11] Sample F represents corn beta amylose, the soluble component of 168-hour ground corn starch after electrophoresis and precipitation.[7] Sample G represents corn starch ground for 168 hours. Sample H represents sample G ground corn starch which had been subjected to an alkali treatment, and reprecipitated out as the stable portion, which in turn was reground for another 140 hours in a small ball mill. Sample I represents corn alpha amylose, the insoluble component of 168-hour ground corn starch after electrophoresis.[10,7] Sample J represents 168-hour ground corn starch, reground another 160 hours in a small ball mill, so that the total time of grinding was 320 hours. Sample K represents corn white dextrin made commercially by spraying whole starch with dilute hydrochloric acid and heating this damp product around 180° for a short period of time.[12] Sample L represents a "thin-boiling" corn starch made by giving whole starch an acid treatment similar to that given Lintner's soluble potato starch.[12] Sample M represents potato starch ground for 500 hours in a ball mill. Sample N represents corn beta amylose made by treatment of corn starch with an alcoholic solution of hydrochloric acid, followed by an ammonium thiocyanate gelatinization.[10]

It is interesting to note that the iodine consuming value after a $N/10$ alkaline treatment is considerably higher than after the treatment with the more concentrated alkali as exemplified by samples as marked in Table II, giving for "C," 11.7 mg.; "F," 26.5 mg.; "G," 25.1 mg.; and "K," 36.5 mg.

(11) Gore, *Ind. Eng. Chem.*, **20**, 865 (1928).

(12) Walton, "A Comprehensive Survey of Starch Chemistry," The Chemical Catalog Co., New York, 1928.

Further, by grinding a corn starch and determining the alkali stable residue from time to time, it has been found that the effect increases with increase in time just as is the case in making "soluble" or "thin-boiling" starches by acid treatment in the cold. In the latter instance, of course the granules are not broken (see Fig. 4).

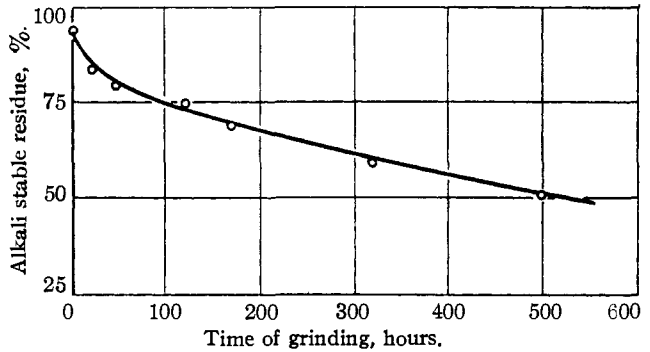

Fig. 4.—Relation between time of grinding of corn starch and amount of alkali stable residue.

The amount of surface exposed to the reagent at first in the case of the ground starch or amyloses is much greater than in the case of the soluble or modified starches where the granules are intact but the reagent soon swells and ruptures the latter, so conditions are about the same soon after the reaction has proceeded for a short time. Even a part of the less easily dispersed corn α-amylose[13,7,10] changes with acid treatment or grinding to give alkali labile material in a manner similar to the corn beta so that in the whole corn starch each of these amyloses is affected by various treatments to give alkali susceptible material. A sample of corn alpha amylose with an initial iodine reduction of 1.6 mg. per 100-mg. sample gave 10.9 mg. of iodine reducing material after a thirty-minute treatment at 100° in 5.4 N alkali.

When drying a sample of neutral ground starch already containing some alkali susceptible material, there was a slight increase in it (or decrease in alkali stable material). For example, when the initial alkali stable residue is 68.0% it changes to 67.0% after four hours, to 62.3% after sixteen hours, and to 61.5% after fifty hours at 105°.

On oven drying moist acidulated starch, which is essentially the process of white dextrin manufacture, there is, however, rather extensive breakdown of the starch, see Table I, item K. Apparently the acid causes this change during the early stages of the treatment when there is still considerable moisture present. Later if the temperature is raised, the white dextrin changes to yellow and a loss of water ensues. Finally no more

(13) Taylor and Lifschitz, THIS JOURNAL, **54**, 1054 (1932).

alkali labile material is formed, but on the contrary any alkali labile material already present is transformed over to *alkali stable*. This is illustrated rather strikingly by an experiment where a "thin boiling" starch containing but 56% alkali stable material (see Table I, Item L) was acidulated and roasted to make a yellow dextrin. This new dextrin contained 86% alkali stable material even though its initial reducing value was 10.6 mg. of iodine per 100 mg. of sample.

A rather large portion of the labile material must have been converted to some kind of stable material and the initial reducing value which normally would indicate a high alkali susceptible portion in an amylose must be in this case due to glucose or maltose or something similar to it for the high alkali susceptible portion does not materialize as it would in an amylose or starch with this initial reducing value. Some studies are being made now on the glucosan types in order to shed more light on these findings because the new stable material is not like the original amylose and synthetic dextrins from levo-glucosan are stable as is levo-glucosan itself toward hot aqueous alkali.

It must be remembered that every starch, amylose or dextrin whether it contains a large or small amount of alkali stable material will hydrolyze practically quantitatively to glucose on boiling with aqueous acid for a sufficient time. All these substances are therefore built up from glucose units whether they are alkali stable or alkali labile.

It is evident that starches and their amyloses may contain relatively large amounts of hydrolytically degraded but still very similar polysaccharides associated with them. While reducing in character this material is not in the main glucose or maltose and not truly water soluble although it may disperse. Pastes made from starches containing much of this material are less viscous than pastes made from the same weight of that same starch which contains but little of the partially broken down alkali-labile material. Such degraded starches are known as "thin-boiling" or "soluble starches." These changes may come about through enzymic attack before the starch is isolated, during the process of manufacture, or may be deliberately brought about by acid treatment as in making soluble starches, etc. The general appearance of the granule is substantially unchanged while these modifications are taking place in the amylose within.

When such partially degraded starches are used to make derivatives or as a substrate for enzyme action, it is probable that the speed and possibly the course of the reaction will be different with the two closely related but chemically different products. Such degraded products are very often employed for experiments on starch, for one of the first operations is often the "solubilizing" of the starch so that the pastes can be handled more conveniently. This lack of homogeneity throws some doubt on the results when these degraded substrates are used.

Another point of interest that develops from this work is the difference between the very alkali labile hydrolytic-type dextrins from the continued attack of the aqueous acid and the very alkali stable yellow dextrins from long roasting of starch. The two types of "dextrins" are obviously not the same chemically.

Summary

1. When a given starch, amylose or dextrin is heated with dilute or concentrated alkali, only a very definite fraction is destroyed by the alkali with a corresponding increase in the reducing value of the system as measured by the hypoiodite method.

2. Starch or amylose which has not been degraded is substantially unaffected by hot aqueous alkali.

3. Two methods are given for quantitatively estimating the portion of starch which is stable toward alkali.

4. Aqueous acid, certain heat treatment or grinding in the presence of moisture are capable of producing a high alkali unstable fraction from a given starch or amylose.

5. Yellow dextrin made by roasting starch contains a large amount of material stable toward alkali.

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The Interaction of Ketene with Aromatic Aldehydes and its Bearing on the Perkin Reaction

BY CHARLES D. HURD AND CHARLES L. THOMAS[1]

Shortly after discovering diphenylketene Staudinger[2] found that it would add to quinone and produce a β-lactone. Ketene itself failed to do this. Hence, this property of addition at carbonyl groups was ascribed to the disubstituted ketenes.

The present work concerns itself with the reaction of ketenes with aromatic aldehydes. From Staudinger's work it would be anticipated that no reaction should occur when ketene was passed into benzaldehyde. None was observed. If, however, a little anhydrous potassium acetate was present, ketene then reacted vigorously with benzaldehyde or furfural or *m*-nitrobenzaldehyde to produce dark colored, viscid liquids.

If the mechanism of the reaction consisted merely in direct addition, β-lactones should have been the major products. They were formed but the chief reaction products were mixed acid anhydrides, namely, cinnamic

(1) Holder of a Quaker Oats Fellowship, 1929–1930, administered through the Miner Laboratories, Chicago.

(2) Staudinger, *Ber.*, **41**, 1355 (1908).